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9 April 1960

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URANYL NITRATE

- USSR -

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NEW YORK 17, N. Y.

JPRS: 2511

CSO: 3822-N/a

ON THE FORMATION OF A COMPLEX COMPOUND OF
URANYL NITRATE

[Following is a translation of an article
written by V. M. Vdovenko, A. A. Lipovskiy,
and M. G. Kuzina in Zhurnal Neorganicheskoy
Khimii (Journal of Inorganic Chemistry),
Vol. 11; No. 4, 1957, pages 970-974.]

The study of the complex processes of formation in nonaqueous solutions has both theoretical and practical aspects. It is known that the formation of a complex compound may greatly affect the extraction of a given element by an organic solvent. There are numerous data in the literature which indicate that the factor of uranium distribution changes with a change in the concentration of the NO_3^- ions during the aqueous phase /1 - 3/. This fact might be connected -- at least to some extent -- with the formation of nitrate complexes of the uranyl ion /4/.

Apparently, there is a possibility of examining the formation and stability of such complexes by means of spectrophotometric methods.

The present report covers the study of the formation of a complex compound of the uranyl ion in acetone, upon the addition of nitrates of pyridine or aniline intended to serve as donors of the NO_3^- ion. The measurements were made with spectrophotometers of the types SF-2m and SF-4. Water-free acetone was used to obtain duplicable data. The processes of dissolving uranyl nitrate in acetone and of making the spectrophotometric measurements were performed in the absence of direct solar light. This precaution was necessary because of the photochemical action of light upon all the solutions of uranyl nitrate that might have induced considerable changes in the optical density of the solutions. In order to eliminate the changes in the concentration of the uranyl nitrate in the solution due to the evaporation of the solvent, the absorption cuvettes were provided with lids fixed in their positions by molten paraffin. Maintaining these precautions made it possible to achieve constant

values for the molar factors of extinction.

Increasing the concentration of $C_5H_5N \cdot HNO_3$ caused considerable variations in the absorption spectrum of the uranyl nitrate solution in acetone (Fig. 1). Analogous changes were also observed when tetrabutylammonium nitrate was used as the complex-former (4).

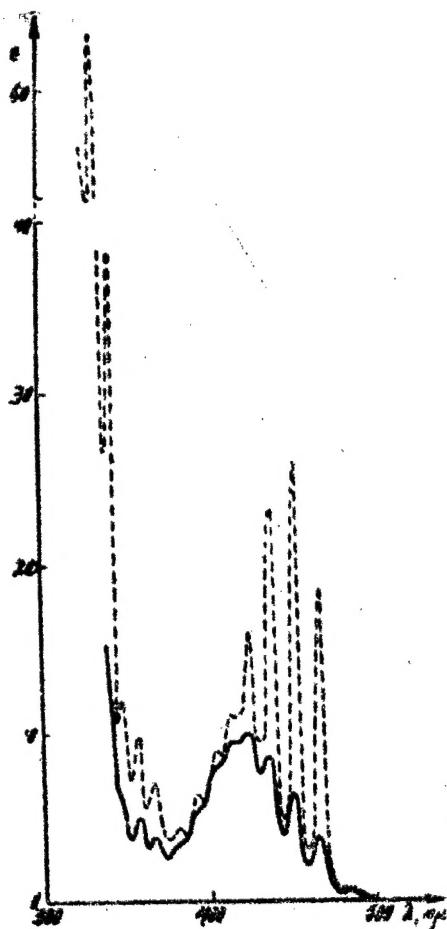


Fig. 1. The absorption spectra of $UO_2(NO_3)_2 \cdot 6H_2O$ (full line) and of $UO_2(NO_3)_2 \cdot 6H_2O + Py \cdot HNO_3$ (dotted line) in acetone.

The composition of the complex thus formed has been established by using the method of Ostromyslenskiy-Zhob. A series of solutions containing various molar ratio of uranyl nitrate to pyridine or aniline nitrate prepared and their absorption spectra was measured. And since in this case the original solution already possessed its own color, the resulting diagram of property-composition was plotted for the excessive optical density (ΔD). To obtain these values, absorption spectra were measured for the corresponding solutions of uranyl nitrate in the absence of the complex-former. These values of extra optical density could also have been obtained by computation from predetermined values of the molar factors of extinction. Results so obtained have shown satisfactory agreement with the results of experimental work.

Fig. 2 presents the results of one series of tests performed for the determination of the complex compound. The complex-former was pyridine nitrate. Quite analogous results were obtained with aniline nitrate. The values of ΔD for the corresponding absorption bands practically coincided in both cases.

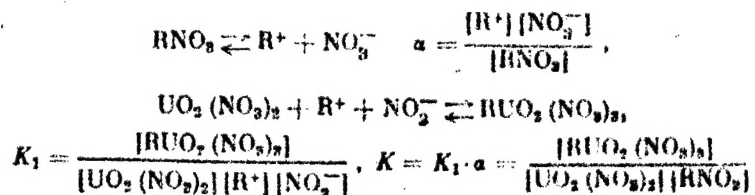
The diagram of property-composition (Fig. 2) shows a definite break at a ratio of 1:1. This applies to all four absorption bands for which changes of optical density during the formation of the complexes are outstanding. Thus, the determination of the composition of the complex thus formed in the solution leads to the conclusion that a complex com-

pound of uranyl trinitrate actually did form.

A series of experiments proceeded with a constant concentration of uranyl nitrate and a variable one of the organic complex-former, in order to obtain data on the stability of the compound so formed. Fig. 3 shows the results of this series of measurements, represented by the relationships between the changes in the molar factors of extinction and the concentrations of the complex-former. The concentration of uranyl nitrate amounted to 0.015 mol.

It is evident that as long as the concentration of the NO_3^- ions, subject to coordination, is insufficient, the molar extinction factor grows steadily in agreement with the complete binding of the uranyl nitrate by the complex. After the whole amount of uranyl nitrate has been so bound, the further addition of the complex-former does not lead to a further increase in the molar extinction factor. Judging from Fig. 2, we can conclude that the complex thus formed had a high stability /5/. In this case, the relationship $\varepsilon = f(C_{\text{NO}_3^-})$ can be extrapolated by two intersecting straight lines. The point of intersection shall correspond to the composition of the complex formed. Values obtained by this graphic extrapolation practically coincide with those determinations of the complex's composition that were obtained by the method of Ostromyslenskiy-Zhob.

The reaction that took place can be represented by the following scheme:



The knowledge of the extinction factors of the absorption bands for uranyl nitrate, and for the complex thus formed, allows us to compute the value of K identifying the stability of that complex. The computation proceeds according to the formula of N. P. Komar:

$$K = \frac{X}{(C_1 - X)(C_2 - X)}$$

where X is the concentration of the complex, C_1 is the total concentration of uranyl nitrate, and C_2 is the total concentration of the complex-former.

The concentration of the complex has been determined for each experiment according to the formula:

$$D = \varepsilon_1(C_1 - X) + \varepsilon_2 X \quad l$$

where ε_1 and ε_2 are the molar extinction factors for the corresponding absorption bands for uranyl nitrate and for the complex of uranyl trinitrate; D is the computed optical density, and l is the length of the cuvette.

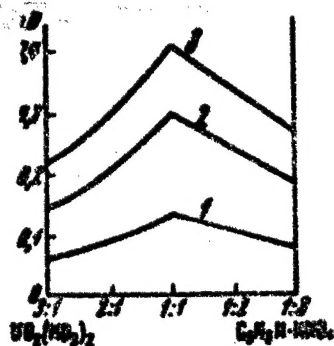


Fig. 2. Graphs used for the determination of the complex's composition:

- 1- $\lambda = 424 \text{ m}\mu$;
2- $\lambda = 467 \text{ m}\mu$;
3- $\lambda = 451 \text{ m}\mu$.

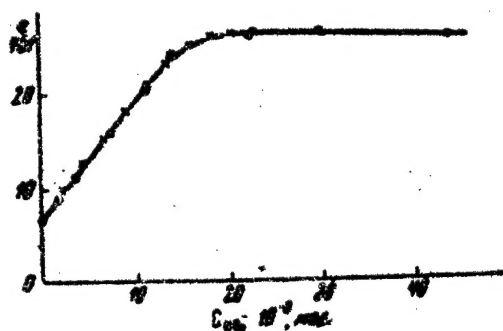


Fig. 3. Changes of E_{451} in relation to the concentration of the complex-former.

O -- tests with $\text{Py} \cdot \text{HNO}_3$

X -- tests with $\text{An} \cdot \text{HNO}_3$

Table 1 shows the numerical values of D obtained in the series of tests with a constant concentration of 0.015 mol of uranyl nitrate. The table contains data obtained by using the values of spectrophotometrical measurements.

Table 1

| Concentration, mol. 10^4 | | | $\lambda = 436 \text{ m}\mu$ $K \cdot 10^{-3}$ | Concentration, mol. 10^4 | | $\lambda = 451 \text{ m}\mu$ $K \cdot 10^{-3}$ |
|-------------------------------------|------------------------------|--------------------------------|---|------------------------------|--------------------------------|---|
| $\text{Py} \cdot \text{HNO}_3$ | $\text{UO}_2(\text{NO}_3)_2$ | $\text{UO}_2(\text{NO}_3)_2^-$ | | $\text{UO}_2(\text{NO}_3)_2$ | $\text{UO}_2(\text{NO}_3)_2^-$ | |
| 22,5 | — | — | — | 130,0 | 20,0 | 6,2 |
| 45,0 | 105,9 | 44,1 | 4,6 | — | — | — |
| 67,5 | 84,5 | 65,4 | 3,7 | 85,7 | 64,9 | 2,9 |
| 90,0 | 63,2 | 86,8 | 4,3 | 62,7 | 87,3 | 5,2 |
| 112,5 | 41,1 | 109,0 | 7,6 | 42,8 | 107,2 | 4,7 |
| 135,0 | 20,3 | 123,7 | 4,2 | 25,9 | 124,1 | 4,4 |
| 157,5 | 12,8 | 137,2 | 5,3 | 12,4 | 137,6 | 5,6 |
| 180,0 | 5,9 | 144,0 | 6,7 | 6,1 | 144,1 | 6,6 |
| Average) $(5,2 \pm 1,1) \cdot 10^3$ | | | | $(5,1 \pm 0,9) \cdot 10^3$ | | |

Thirty-two tests using pyridine nitrate as a complex-former with variable starting concentrations of uranyl nitrate yielded for K the value $(4.8 \pm 1.1) \cdot 10^3$. In the case of aniline nitrate, K was found to be $(3.6 \pm 0.7) \cdot 10^3$.

It is obvious that the two values of K agree within the possible error of the determination. This conclusion could be reached directly from Fig. 1, and it indicates that the constants of dissociation in the solutions of pyridine and aniline nitrate in acetone are sufficiently close.

The rather high magnitude of error estimated for the value of K is due to the difficulty of computing the increases in optical density of the solutions with the necessary precision.

One of the important factors affecting the stability of the complex of uranyl trinitrate thus formed consists in the competition for electron-donorship between the molecules of the solvent and of water each tending to form the corresponding solvates. The NO_3^- groups can also act as electron donors substituting for the other solvating molecules when the concentration of these groups rises. The effect of the solvent type, and of its content of water, results as well in a variation of the medium's dielectric constant. An addition of water raises the dielectric constant and also raises the degree of the complex's dissociation. In addition, water is known to be a virogous donor of electrons and can substitute for the NO_3^- groups, even when the values of the dielectric constant are not very high.

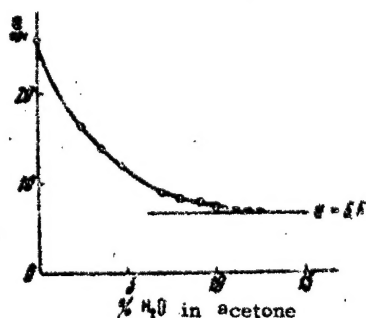


Fig. 4. Change of E_{451} in relation to the concentration of water in acetone. The full line parallel to the abscissa corresponds to E_{451} in water.

This circumstance is likely to cause differences in the stability of $[\text{UO}_2(\text{NO}_3)_3]^-$ in various organic solvents. Thus, the value of K characterizing the stability of the complex compound of uranyl trinitrate was found to be as low as

9.8 \pm 2.0 when cyclohexanone was substituted for acetone. When ethyl alcohol is used as a solvent, a complex formation hardly takes place even with a high excess of pyridine nitrate.

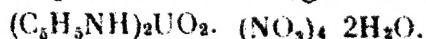
Table 2

| Content of U, % | Content of NO ₃ , % | Content of C ₅ H ₅ N, % |
|-----------------|--------------------------------|---|
| 33,71 | 33,20 | 22,50 |
| 34,19 | 35,83 | 22,30 |
| 34,50 | 34,31 | 22,70 |
| 34,56 | 31,54 | — |
| 34,29 | 34,98 | — |
| 33,07 | 34,61 | — |
| 33,90 | 35,61 | — |
| Average 34,03 | 34,16 | 22,50 |

The effects of the change in the conditions of existence of the complex of uranyl trinitrate dissolved in acetone can be clearly observed from the diagram in Fig. 4. It shows that the presence of 10 percent water in the acetone solution practically prevents the formation of the complex*.

By adding benzene to the acetone solution of $[\text{UO}_2(\text{NO}_3)_3]^-$, we obtained a solid phase representing a yellowish green fine-crystalline precipitate. This was analyzed for pyridine, uranium and the NO_3^- group. Uranium was determined as usual by precipitating it with ammonia from an aqueous solution, followed by igniting with U_3O_8 . Pyridine was determined by Bauer's method [7], argentometrically. The NO_3^- group was precipitated by nitron from approximately 1N solutions in sulfuric acid. The precipitate was dried at 110°C. Results are given in Table 2.

The table's data indicate that the ratios of U/NO_3^- and U/Py are almost precisely 1/4 and 1/2. One atom of uranium calls for four NO_3^- groups and for two molecules of pyridine. On the precipitation from the solution in acetone, pyridine was no longer detected. The absence of acetone in the washed-and-dried precipitate was proved by the hydroxyl-amine reaction. The analytical data and the circumstances thus cited allowed us to establish the composition of the complex. This compound can be given the formula



*The presence of a horizontal segment in the curve indicating the relation between the optical density of the solution and the concentration of the complex cannot be considered to be decisive evidence for the complete binding of the central ion into a complex compound.

Theoretical and experimental data characterizing the composition of the compound are:

Found: %: U — 34.03; Py — 22.50; NO_3^- — 34.16
Computed: %: U — 33.33; Py — 22.13; NO_3^- — 34.73

We found no data in the literature regarding the formation of this kind of a salt. It should be noted that it is insoluble in both ethyl and dibutyl ethers.

The size of this report makes it impossible to indulge in a more or less detailed discussion of the character of variations in the absorption spectrum of uranyl nitrate resulting from the formation of the complex compound of uranyl trinitrate. It is to be noted that only a part of the wave components of the absorption band is substantially pronounced in the absorption spectrum of the complex compound of uranyl trinitrate.

It should be further noted that the interpretation of the variations given in the report by Kaplan et al /4/ demands elucidation, for the authors did not measure the changes in the absorption spectra for the regions of waves below $350\text{m}\mu$. On making these computations, we discovered that the formation of the complex of uranyl trinitrate is accompanied by the appearance of a regular structure upon the background of the strong absorption bands in this part of the spectrum.

Conclusions

1. The formation was investigated of a complex compound of uranyl in acetone when the nitrates of aniline or pyridine are used in the capacity of donors of the NO_3^- groups. The composition of the complex has been established spectrophotometrically, and the constant characterizing its stability has been computed.

2. It was demonstrated that the stability of the complex compound of uranyl trinitrate depended on the nature of the solvent and on the content of water in the organic phase.

3. A new compound of the nitrates of pyridine and uranyl has been separated and analyzed. The composition can be presented by the empirical formula

4. A regular structure has been detected on the background of complete absorption in the ultraviolet part of the absorption spectrum of the complex thus formed.

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Received by the Editors
1 December 1956.

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